Long-range Coupling in the Proton Nuclear Magnetic Resonance Spectra of Some Benzothiophen and Benzofuran Analogues

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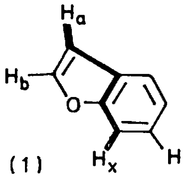
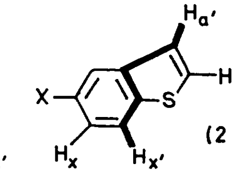
The ^{1}H n.m.r. spectra of benzo[1,2-*b*:4,3-*b*′]difuran, benzo[1,2-*b*:4,3-*b*′]dithiophens, and thieno[3,2-*e*]benzofuran are discussed in the light of a possible five bond long-range coupling. The photocyclisations of 1-(5-bromo-2-thienyl)-2-(2-thienyl)ethylene and 1-(5-chloro-2-thienyl)-2-(2-thienyl)ethylene gave benzo[1,2-*b*:4,3-*b*′]dithiophen and 7-chlorobenzo[1,2-*b*:4,3-*b*′]dithiophen respectively.

LONG-RANGE inter-ring proton–proton spin coupling has been observed in a number of compounds.[1-4] Elvidge and Foster [1,2] have investigated this type of long-range coupling in indene, benzo[*b*]furan (1), and benzo[*b*]thiophen (2a) and have conclusively shown that it arises from a five bond coupling between the 3- and 7-protons and not the 2- and 7-protons in each case. The zig-zag path indicated in (1) is suggested as being favourable for such couplings. Further work by Black and Heffernan [3] and Caddy and his co-workers [4] on benzothiophen and benzofuran derivatives indicates that the magnitude of coupling is small, *i.e. ca.* 0·6 to 1·0 Hz for most derivatives. They attribute their inability to measure the exact couplings in some derivatives to the fact that splittings of 0·5 to 0·6 Hz are near the limit of resolution of the instrument used. However, in such cases they suggest there is a long-range coupling on the basis of the line widths being of the same order as the line widths of similarly resolved resonances.

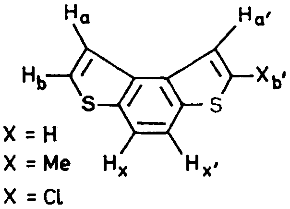


(1)

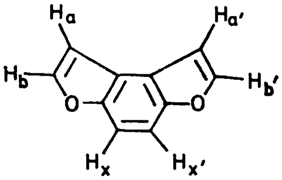


(2) a; X = D
b; X = Cl

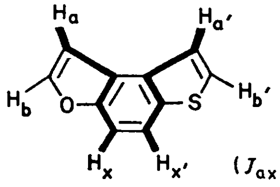
Benzo[1,2-*b*:4,3-*b*′]dithiophens (3a—c), benzo[1,2-*b*:4,3-*b*′]difuran (4), and thieno[3,2-*e*]benzofuran seem to be particularly favourable cases [5] in which to look for such long-range couplings since the molecules have few protons not involved in the coupling and the favourable zig-zag path is present. The spectra of compounds (3) and (4) are compared with the spectra of benzofuran (1) and benzothiophens (2a and b) in the Table.



(3) a; X = H
b; X = Me
c; X = Cl



(4)



(5)
(J_{ax} = 0·8 Hz; $J_{a'b'}$ = 0·6 Hz)

Long-range couplings are observed in the spectra of 7-methyl- and 7-chloro-benzo[1,2-*b*:4,3-*b*′]dithiophens (3b and c) and thieno[3,2-*e*]benzofuran (5) but are not

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[1] J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 1963, 590.

[2] J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 1964, 981.

[3] P. J. Black and M. L. Heffernan, *Austral. J. Chem.*, 1968, **18**, 353.

[4] B. Caddy, M. Martin-Smith, R. K. Norris, S. T. Reid, and S. Sternhell, *Austral. J. Chem.*, 1968, **21**, 1853; S. Sternhell, *Quart. Rev.*, 1969, **23**, 258.

[5] C. E. Loader and C. J. Timmons, *J. Chem. Soc.* (*C*), 1967, 1677.

apparent in benzo[1,2-*b*:4,3-*b'*]dithiophen (3a) and benzo[1,2-*b*:4,3-*b'*]difuran (4). The chemical shifts of individual proton resonances and the resolution of these resonances appear to be affected markedly by the solvent and, in general, better resolved spectra are obtained in perdeuteriobenzene rather than in carbon tetrachloride.

General features of their spectra are that the resonances of the furan protons appear as an AX system with coupling constants *ca.* 2·1 Hz,[6] the resonances of the thiophen protons appear as an AB system with coupling constants in the range 5·4—5·6 Hz,[6] and the resonances of the benzenoid ring protons in the unsymmetrical benzodithiophens and thienobenzofuran appear as an AB system with coupling constants in the range 8·6—9·0 Hz, which are in good agreement with those expected between *ortho*-protons in a benzene ring.[6]

TABLE

^{1}H N.m.r. spectra of some benzothiophens and benzofurans

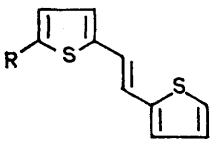
Compound	Solvent	Proton resonances (τ) H_a	H_b	H_x	$H_{a'}$	$H_{b'}$	$H_{x'}$	Coupling constants (Hz) J_{ab}	J_{ax}	$J_{a'b'}$	$J_{a'x'}$	$J_{xx'}$
(1) [3]	CCl_4	3·34	2·48	2·58			2·80	2·1	0·8			8·35
(2a) [4]	$CDCl_3$			2·66	2·67	2·57	2·12			5·6	*	8·5
(2b) [4]	$CDCl_3$			2·73	2·78	2·56	2·27			5·6	0·75	8·6
(3a)	CCl_4	2·43	2·58	2·30				5·5				
	C_6D_6	2·71	2·93	2·60				5·4				
(3b)	CCl_4	2·53	2·63	2·39	2·78		2·43	5·5	0·6		*	9·0
	C_6D_6	2·67	2·94	2·61	3·02		2·61	5·45	*		*	8·8
(3c)	CCl_4	2·56	2·58	2·33	2·60		2·50	5·55	*		0·6	8·7
	C_6D_6	2·96	3·03	2·73	2·96		3·00	5·5	0·7		0·7	8·7
(4) †	CCl_4	3·10	2·32	2·57				2·1				
(5)	CCl_4	3·06	2·38	2·55	2·56	2·56	2·35	2·1	0·8		*	8·9
	C_6D_6	3·38	2·76	2·69	2·79	2·92	2·61	2·15	0·6	5·5	0·6	8·6

* Resolution of instrument insufficient to determine spacing but line widths suggest splitting of the same order as the remainder of the series. † Run on a Perkin-Elmer R10 spectrometer at 60 MHz.

Similar spectral data have been presented by Kellogg and his co-workers[7] for compounds (3a), (4), and (5). Like us they observe no apparent long-range couplings in the symmetrical benzo[1,2-*b*:4,3-*b'*]-difuran and -dithiophen and observe one long-range coupling in the unsymmetrical thieno[3,2-*e*]benzofuran. This latter coupling they associate with the furan part of the molecule. We note however that an additional long-range coupling of 0·6 Hz, which is associated with the thiophen part of the molecule, is observed in the perdeuteriobenzene solution spectrum of thieno[3,2-*e*]benzofuran (5). Two long-range couplings are also observed in the perdeuteriobenzene solution spectrum of 7-chlorobenzo[1,2-*b*:4,3-*b'*]dithiophen.

The inability to decipher a long-range coupling in both symmetrical molecules (3a) and (4) appears to be associated with the equivalence of the benzenoid protons. This also appears to be the case in the perdeuteriobenzene solution spectrum of 7-methylbenzo[1,2-*b*:4,3-*b'*]-dithiophen (3b) in which the benzenoid protons are practically equivalent. The inability to resolve couplings in these cases may be due to virtual coupling[8] which may lead to a masking of such long-range couplings.

An interesting outcome of the attempted preparations of 7-halogeno-derivatives of benzodithiophen is the lack of formation of a 7-bromo-derivative. Irradiation of the 1-(5-bromo-2-thienyl)-2-(2-thienyl)ethylene (6a) gives solely the unsubstituted benzodithiophen (3a). However, irradiation of 1-(5-chloro-2-thienyl)-2-(2-thienyl)ethylene (6c) gives the required 7-chloro-derivative (3c) in good yields. This outcome is not totally surprising because C–Br bonds in bromothiophens are known to be easily cleaved.



(6) a; R = Br
b; R = Me
c; R = Cl

The photocyclisation of 1-(5-methyl-2-thienyl)-2-(2-thienyl)ethylene (6b) gives, as expected, 7-methylbenzo[1,2-*b*:4,3-*b'*]dithiophen (3b).

EXPERIMENTAL

The reaction conditions and apparatus have been previously described.[9] ^{1}H N.m.r. spectra were measured using a Varian HA100 spectrometer at 100 MHz on 8% solutions of the compounds in carbon tetrachloride and perdeuteriobenzene with 3% tetramethylsilane as the internal lock signal. The resolution of the instrument was checked regularly according to the manufacturer's instructions on a 30% solution of *o*-dichlorobenzene in carbon tetrachloride and was *ca.* 0·43 Hz. Spin decoupling experiments, when necessary, were performed using a Muirhead–Wigan Decade Oscillator D-890-B.

trans-1-(5-*Bromo*-2-*thienyl*)-2-(2-*thienyl*)*ethylene* (6a).—This compound was prepared from a Wittig reaction[9] involving 5-bromothiophen-2-carbaldehyde[10] (14 g) and the salt (30 g) formed from triphenylphosphine and chloro-

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[6] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, London, 1965, vol. 2, p. 789.

[7] R. M. Kellogg, M. B. Groen, and H. Wynberg, *J. Org. Chem.*, 1967, **32**, 3093.

[8] J. D. Roberts, R. P. Lutz, and D. R. Davis, *J. Amer. Chem. Soc.*, 1961, **83**, 246; D. R. Davis and J. D. Roberts, *J. Amer. Chem. Soc.*, 1962, **84**, 2252.

[9] E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc.* (*C*), 1968, 1576.

[10] S. Gronowitz, *Arkiv Kemi*, 1955, **8**, 87.

methylthiophen.[11] The product was chromatographed on a silica-gel column with benzene as eluant. Recrystallisation from ethanol gave the *ethylene* (10 g, 50%), m.p. 61—62° (Found: C, 44·2; H, 2·8; Br, 29·1. $C_{10}H_7BrS_2$ requires C, 44·3; H, 2·6, Br, 29·5%); $\nu_{\text{max.}}$ (ethanol) 38,400, and 28,500 cm^{-1} (ε 5700, and 31,500); $\nu_{\text{infl.}}$ 29,600 and 27,600 cm^{-1} (ε 27,200 and 23,600); $\nu_{\text{max.}}$ (KBr) 706(vs), 737(w), 785(m), 794(s), 813(s), 853(m), 941(vs), 963(m), 1042(w), 1052(w), 1076(w), 1124(w), 1180(w), 1214(w), 1223(w), 1265(w), 1280(w), 1329(w), 1359(w), 1412(m), 1438(s), 3015(w), and 3098(w) cm^{-1}. Only the high-field part of the olefinic AB system was observable in the ^{1}H n.m.r. spectrum (J_{AB} 14 Hz).

Irradiation of Compound (6a).—The dithienylethylene (0·5 g) was irradiated in cyclohexane (2 l) with a Pyrex filter for 11·5 h. Chromatography on an alumina column which was eluted with 10% ether–light petroleum and recrystallisation from light petroleum gave only benzo[1,2-*b*:4,3-*b*′]dithiophen (3a) (0·18 g, 50%) with u.v., i.r., ^{1}H n.m.r., and m.p. identical with an authentic specimen. The m.p. was undepressed upon admixture with the authentic compound.

trans-1-(5-*Chloro*-2-*thienyl*)-2-(2-*thienyl*)*ethylene* (6c).—This compound was prepared by a Wittig synthesis from 5-chlorothiophen-2-carbaldehyde[12] (11·1 g) and thienyltriphenylphosphonium chloride (30 g). The product was distilled and 3 g of aldehyde was recovered. The *ethylene* was distilled (180—185°/5 mmHg) and recrystallised from light petroleum as needles (7 g, 41%), m.p. 70—71° (Found: C, 53·1; H, 3·2; Cl, 15·4. $C_{10}H_7ClS_2$ requires C, 53·0; H, 3·1%; Cl, 15·7%) $\nu_{\text{max.}}$ (ethanol) 39,100 and 28,900 cm^{-1} (ε 5700 and 30,300); $\nu_{\text{infl.}}$ 30,000 and 27,700 cm^{-1} (ε 26,100 and 22,600); $\nu_{\text{max.}}$ (KBr) 705vs, 738w, 768w, 790s, 813s, 856m, 941vs, 995s, 1045m, 1065m, 1180m, 1218m, 1269w, 1320w, 1337w, 1362w, 1419m, 1444s, 1506w, 1531w, 3024w, 3078w, and 3098 cm^{-1}.

7-*Chlorobenzo*[1,2-b:4,3-b′]*dithiophen* (3c).—1-(5-Chlorothienyl)-2-(2-thienyl)ethylene (0·97 g) was irradiated in cyclohexane (2 l) containing iodine (100 mg) for 9 h with a Pyrex filter. The product was chromatographed on an alumina column which was eluted with 10% ether in light petroleum. Recrystallisation of the *benzodithiophen* gave needles (0·57 g, 59%), m.p. 63—63·5° (Found: C, 53·5; H, 2·2; Cl, 15·7; S, 28·5. $C_{10}H_5ClS_2$ requires C, 53·5; H, 2·2; Cl, 15·8; S, 28·5%). $\nu_{\text{max.}}$ (ethanol) 39,400, 38,300, 37,100, 34,200, 32,900, and 31,200 cm^{-1} (ε 5100, 14,200, 12,100, 21,600, 16,600, and 3300); $\nu_{\text{infl.}}$ 41,900 and 35,200 cm^{-1} (ε 15,900 and 15,000), $\nu_{\text{max.}}$ (KBr) 699s, 759s, 780s, 830vs, 891w, 899m, 925w, 943w, 1006s, 1088m, 1148s, 1185m, 1201w, 1339w, 1399m, 1500m, and 3074w cm^{-1}.

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[11] K. B. Wiberg in *Org. Synth.*, Coll. Vol. III, 1955, 811.

[12] G.P. 953,082 (*Chem. Abs.*, 1959, **53**, 8163e).